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A STUDY OF LASER ABSORBER IR282 IN PLASTIC AND LIQUID MEDIA

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EMMANUEL A. LUCIA

SEPTEMBER 1977

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
WEAPON SYSTEMS LABORATORY
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A PMMA Air Force visor with 1.06μ absorber IR282 and .53μ absorber K283 was studied for its utility as a laser protective material. The visor material was found to have an optical density~6 at 1.06μ and~4 at .53μ with an luminous transmittance of 44%. More bleaching was observed at high irradiance levels for IR282 in PMMA than in MMA. Pulse narrowing effects were noted and taken into account for the optical density calculations. An explanation is given for the shape of the transmitted pulse.

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INTRODUCTION

This study (supported by the Research in Signal Detection and Low Energy Lasers Program, AH46) was proposed and pursued because of the Army's continuing need for adequate laser protective materials. Some of the difficulties associated with the eye and sensor protective materials are that the absorbers are broadband, the luminous transmittance is too low (<40%), the absorbers bleach under high powers, and the plastic host materials tend to abrade too easily. As protection is built in for more wavelengths the luminous transmittance decreases. The problem becomes even more acute when one of the wavelengths is doubled Nd (.53μ) because this wavelength is very close to the peak of the eye sensitivity curve. This study concerns a material (IR282 with K283 in polymethylmethacrylate [PMMA]) which has an optical density (OD)*~6 at 1.06μ and ~4 at .53μ. The luminous transmittance is 44%. The current Army goggle is made from BG-18 glass for protection against Nd and Ruby lasers but not for doubled Nd lasers.

One of the advantages of the plastic materials is that they can be cast easily into a variety of configurations. In fact one of the samples used in this study has been cast into an Air Force pilot's visor by American Cyanimid Corporation. Frankford Arsenal was provided sample visors as well as the dye IR282 for investigative purposes. The visor material in its original form as well as thinned samples were studied. The dye IR282 was dissolved in methylmethacrylate monomer (MMA) and the same parameters as in PMMA were investigated. In this report, data will be presented for the optical density vs. irradiance levels in MMA and PMMA in both the nanosecond and picosecond time frames. Additionally, pulse narrowing and distorting effects will be discussed.

BACKGROUND

In a previous report[1] the effects of various solvents on the absorption characteristics of IR282 were given. It was found that the peak absorption wavelength shifts and the oscillator strength varies for the different solvents. In PMMA, the peak absorption occurs at 1.002μ with an extinction coefficient of 3.2×10^4 ℓ/mole cm. The absorption spectra for the visor material is shown in Figure 1. The absorption in the green and blue arises from K283 which is also incorporated into the PMMA.

The molecular structure of IR282 is given in Figure 2. This molecule is very similar to many of the other dye molecules developed for 1.06μ absorption. It is stable when incorporated into PMMA. The bleaching which occurs is reversible. The transition responsible for infrared absorption in IR282 involves the excitation of an electron from a π bonding to a π* antibonding molecular orbital.

*Optical density (O.D) = $\log_{10} I_o/I_t$ where I_o and I_t are the incident and transmitted light intensities, respectively.

[1] J. J. Mikula, W. G. Thomas, F. D. Verderame, FA Report R-1984, November 1970.

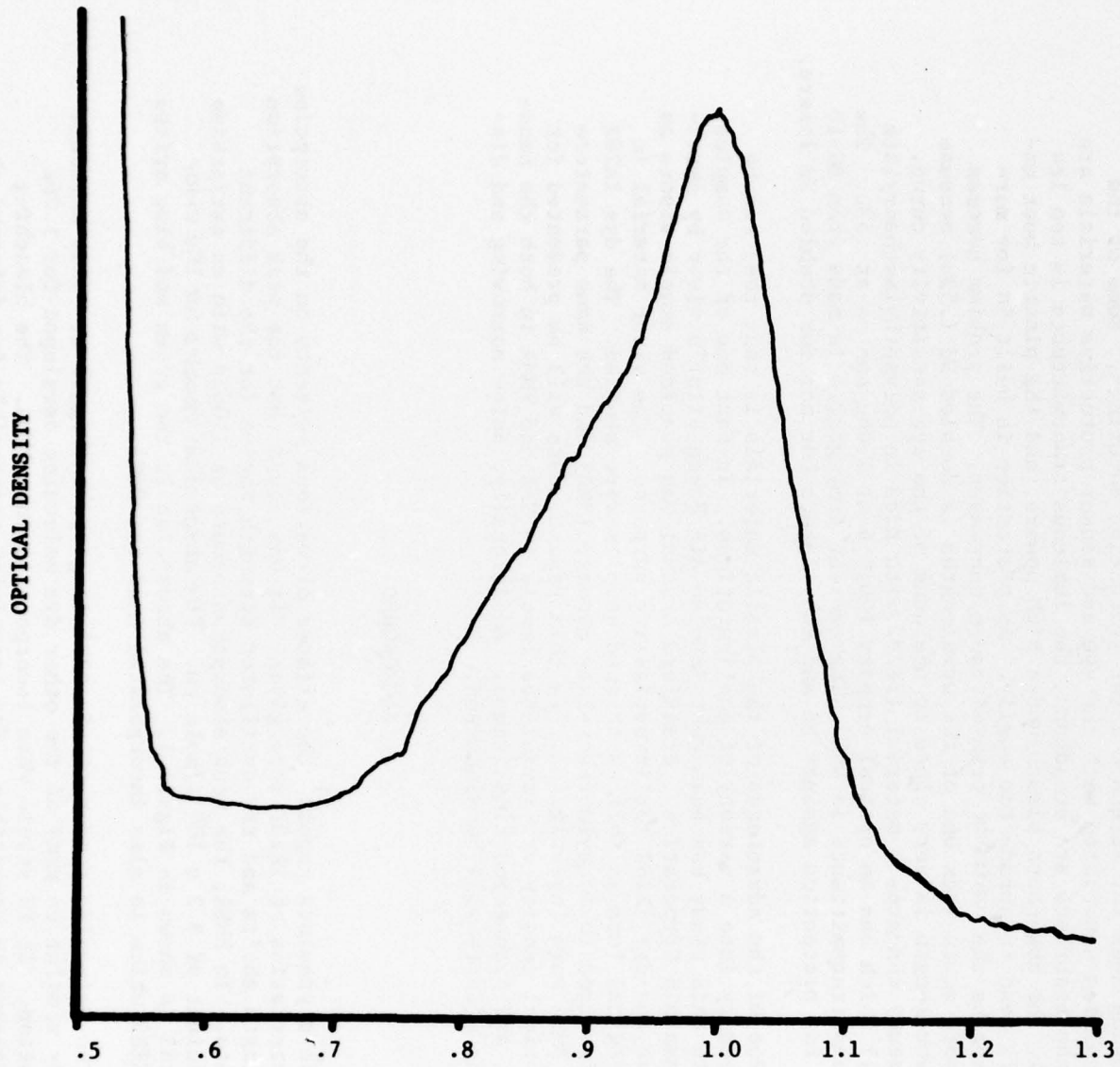

FIGURE 1. THE ABSORPTION SPECTRA OF THE IR282 AND K283 VISOR MATERIAL

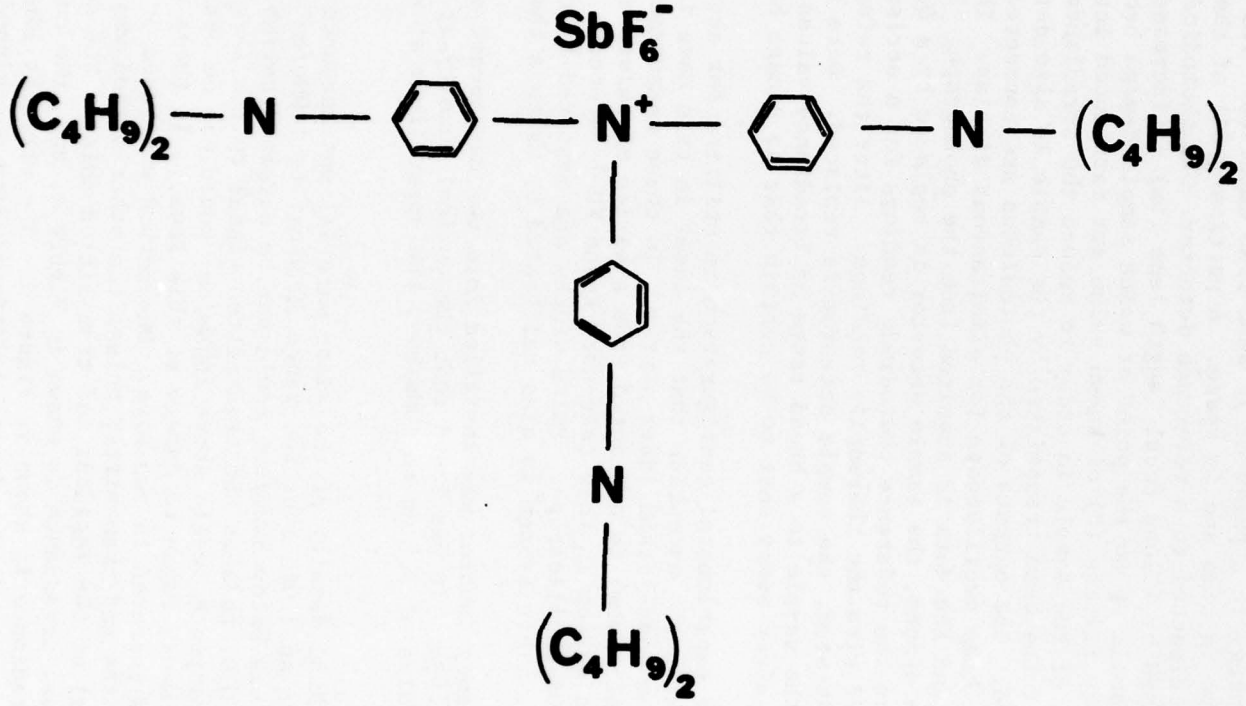

FIGURE 2. THE MOLECULAR STRUCTURE OF IR282

EXPERIMENTAL PROCEDURE

A diagram of the Q-switched 1.06μ laser apparatus is shown in Figure 3. The laser is a Korad K-2 neodymium system which provides approximately 2 joules of energy in a pulse of 17 nsec fwhm duration. The pulse has a smooth envelope in time and in space. A portion (~8%) of the main beam is split off and directed to a reference detector (OTI photodiode). The main beam is focussed by a long focal length lens (1m) to increase the illuminance at the sample up to the point at which sample damage becomes evident. Neutral density filters (F) of known value are introduced into the laser beam in front of the sample in order to reduce the irradiance at the sample. The portion of the beam transmitted by the sample is also detected by an OTI photodiode. The outputs of the photodiodes are connected to a Tektronix Type 556 dual beam oscilloscope for simultaneous display. The tracings are photographed and the data is acquired from the photograph. In order to calibrate the system, the sample detector is replaced by a Quantronix 501 thermopile and the reference photodiode readings for a series of laser shots are correlated with the thermopile readings. After the reference detector has been calibrated, the sample detector is replaced. Data is then obtained by exposing the sample to a broad range of irradiance values. The sample is inspected after every shot to be certain that no damage has occurred.

The same experimental configuration is utilized for acquiring the picosecond data with the exception that the laser in this case is the Korad K-1500 neodymium mode-locked laser system. In these measurements, a single pulse (~18 psec fwhm) is extracted from a series of pulses and amplified. The detection system in this case uses Korad KD-1 detectors connected to a Tektronix 7904 oscilloscope. Pulse widths are measured by two photon fluorescence. This system is also calibrated by using a thermopile.

A frequency doubler was installed into the nanosecond system for measurement at .53μ. It was found that the optical density at .53μ stayed constant at a value of 3.7 up to 10Mw/cm^2, the upper limit at which data was obtained.

The optical density of the visor material was measured as a function of irradiance at 1.06μ over the range 30Mw/cm^2 to 160Mw/cm^2. Data for irradiance values below 30Mw/cm^2 could not be obtained reliably because the high sample O.D. reduces the transmitted signal to the level of the noise. Data for irradiance levels above 160Mw/cm^2 could not be obtained because the plastic media began to damage at this level. In these experiments the O.D. was measured in two ways. One method was based on the peak power of the incident and transmitted pulse; the other method was based on the energy (area) of the incident and transmitted pulse. The curve of the peak power O.D. vs. irradiance is shown in Figure 4; and, the curve of the energy O.D. vs. irradiance is shown in Figure 5. The straight lines are the least squares fit to the data points. Additional data on thinned visor material shown in Figure 6 will be discussed later. From Figures 4 and 5, it is evident that some sample bleaching takes place at high irradiance values. However, it is also clear that the bleaching is not catastrophic; and that, even at irradiance levels extremely unlikely outside of the laboratory (160Mw/cm^2) the visor has an energy O.D. > 5.8.

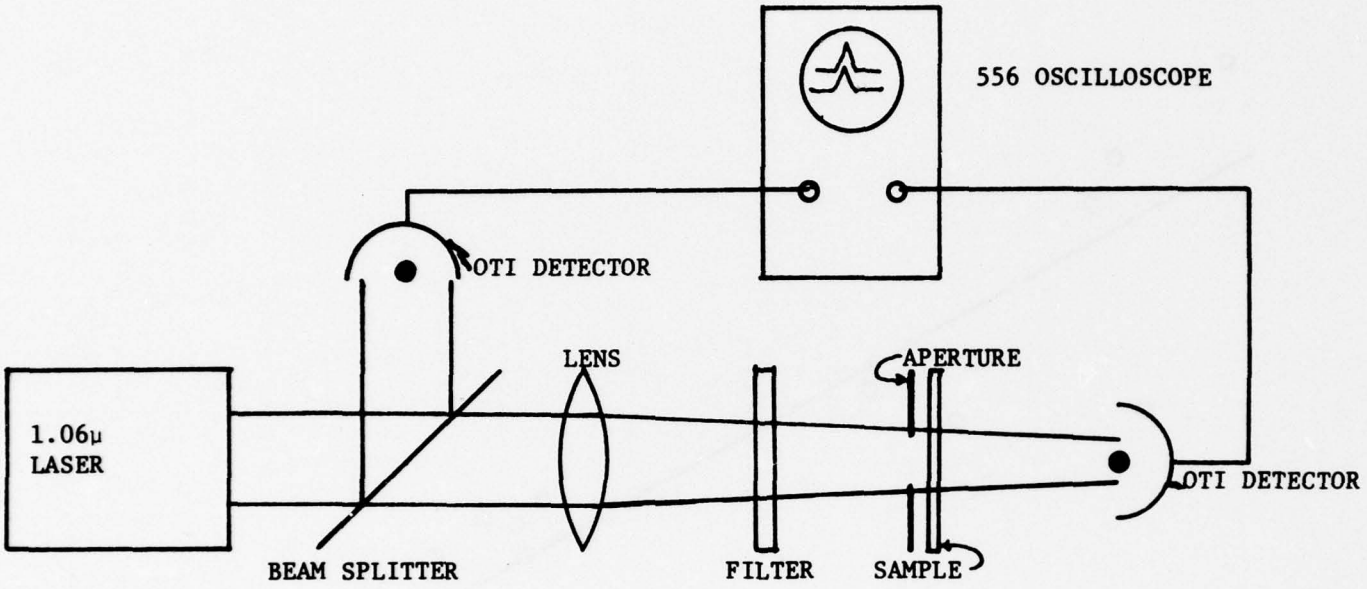

FIGURE 3. A SCHEMATIC DIAGRAM OF THE 1.06u Q-SWITCHED LASER APPARATUS

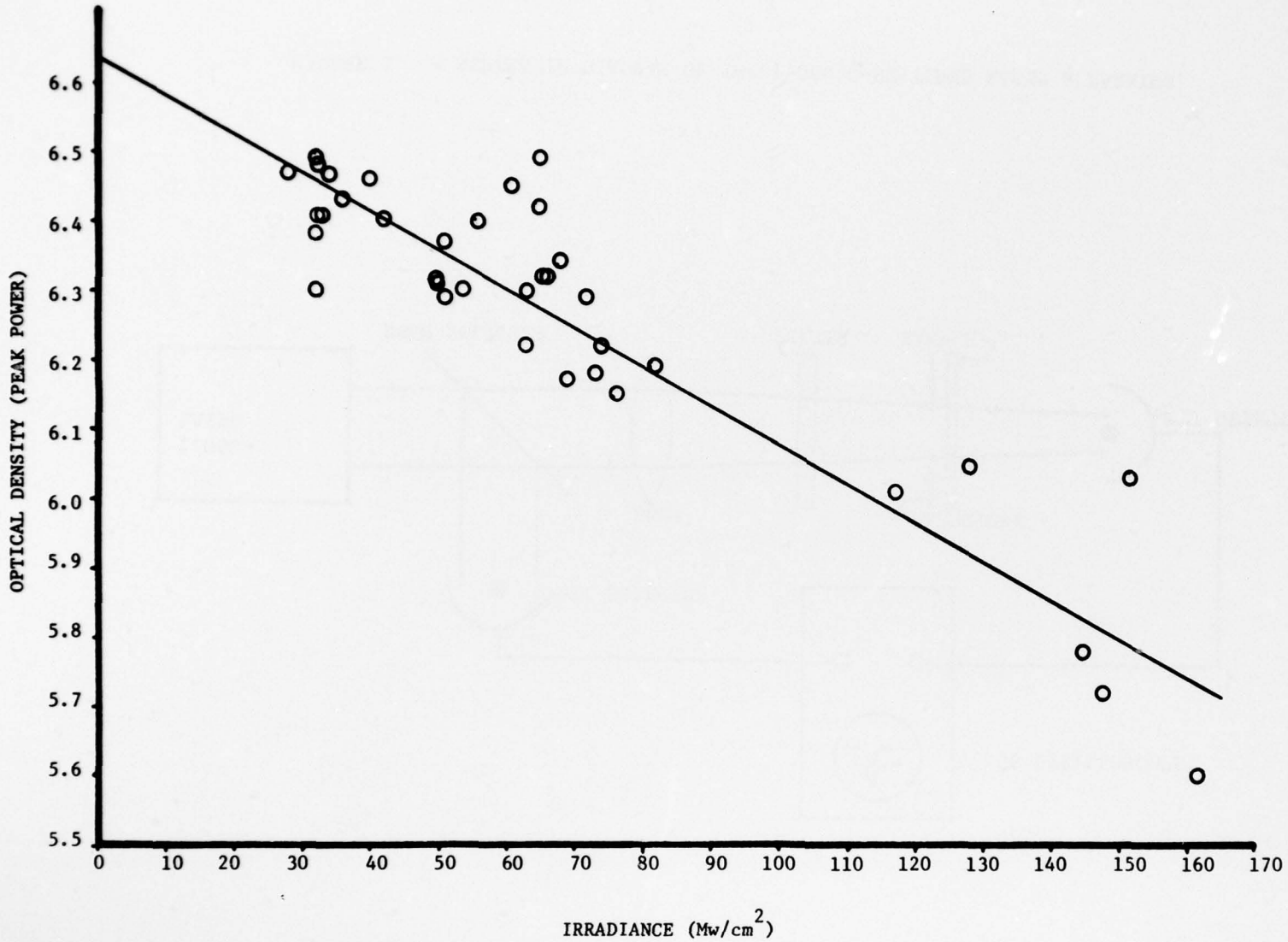

FIGURE 4. THE PEAK POWER OPTICAL DENSITY OF THE VISOR IS SHOWN GRAPHED AGAINST A RANGE OF IRRADIANCE VALUES

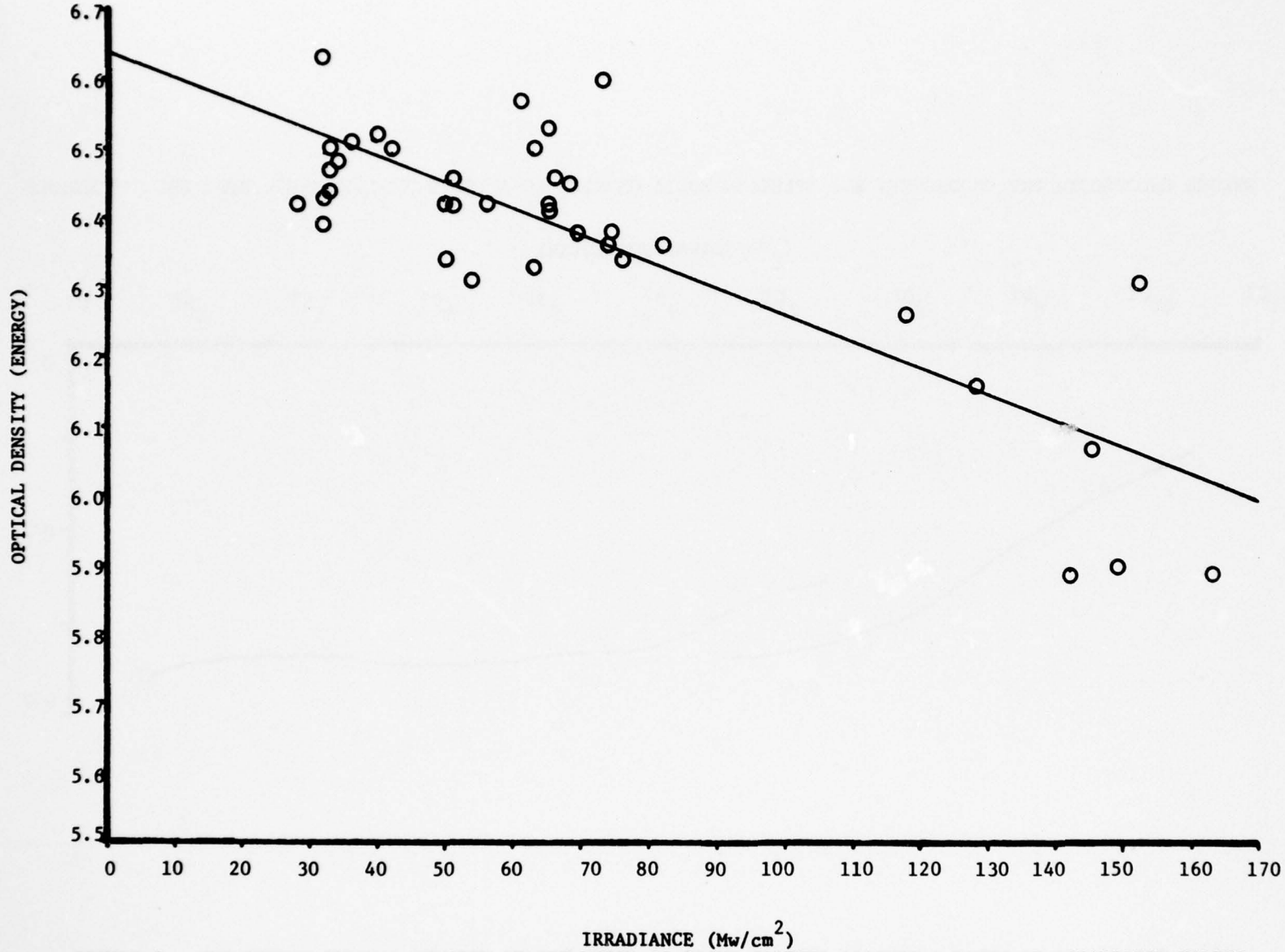

FIGURE 5. THE ENERGY OPTICAL DENSITY OF THE VISOR IS SHOWN GRAPHED AGAINST A RANGE OF IRRADIANCE VALUES

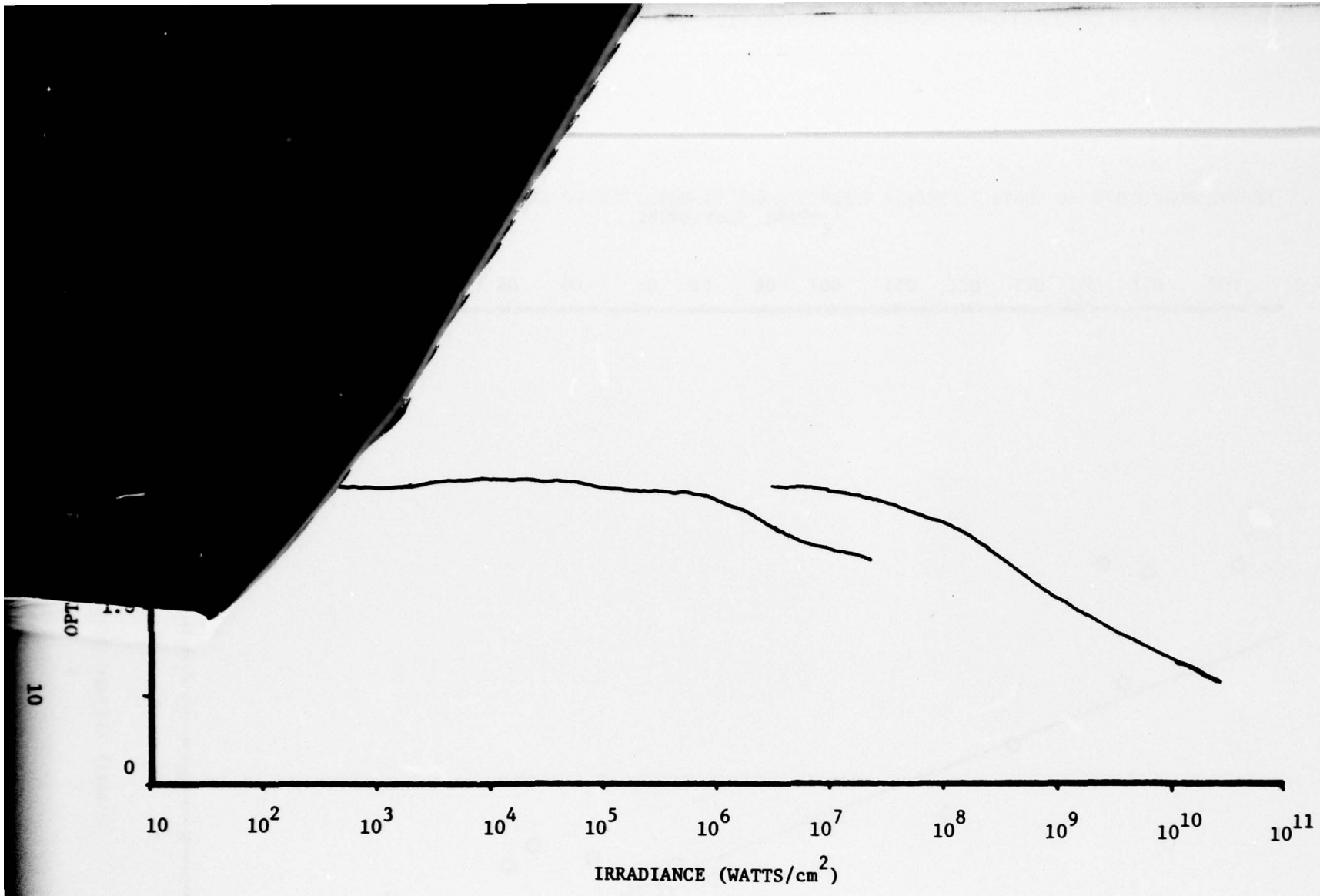

FIGURE 6. THE PEAK POWER OPTICAL DENSITY OF THINNED VISOR MATERIAL FOR NANOSECOND AND PICOSECOND PULSES

DISCUSSION

There are several features of significance in comparing Figures 4 and 5. One feature is that the peak power O.D. falls off faster with irradiance level than the energy O.D. The slope of the peak power optical density curve is $-.0056 \pm .0004$ as compared with $-.0038 \pm .0004$ for the energy optical density curve. This is to be expected because the sample undergoes bleaching which lowers the peak power optical density; and, pulse narrowing occurs which raises the energy optical density value. Another expected feature which appears is that both optical densities have the same extrapolated zero irradiance value ($6.64 \pm .03$). This should clearly be the case as at low irradiance levels no bleaching and no pulse narrowing occur.

The peak power O.D. vs. irradiance for IR282 in MMA is shown in Figure 7 and the energy O.D. data is shown in Figure 8. In comparing Figures 7 and 8, we again find that the peak power O.D. curve has a more negative slope ($-.0007 \pm .0002$) than the energy O.D. curve ($-.00004 \pm .0001$). And, the extrapolated zero irradiance optical density values are the same ($3.77 \pm .02$).

In comparing the optical densities in Figures 4 and 5 with those in Figures 7 and 8, it is found that there is significantly more bleaching in the polymer than in the monomer. This would indicate a significant difference in the excited state to ground state relaxation times in the two media; a clear suggestion for a future experiment to be performed with our picosecond laser system. The relaxation time effect can be seen in Figure 6. Comparing the nanosecond data on the left side of Figure 6 with the picosecond data on the right it is found that the same bleaching level is attained by a picosecond pulse of 1/50 the energy (i.e., number of photons) of the nanosecond pulse. This result is a manifestation of the ground state recovering less during the 18 picosecond pulse than during the 18 nanosecond pulse. The dynamical properties of a multiple level absorber system will not be pursued here.

Two simultaneous oscilloscope traces which reveal the incident and transmitted pulse shapes are shown in Figure 9. The experiment is arranged so that the pulses are coincident when the sample is replaced by a neutral density filter. The sample used for Figure 9 is the visor material; and, the peak irradiance is $142 Mw/cm^2$. The shape of the transmitted pulse shown in Figure 9 is representative of those seen at high powers in the visor material. The transmitted pulse evolves continuously from being very similar in shape to the incident pulse at $30 Mw/cm^2$ (usually narrowed by 0-2 nanoseconds) to the shape of the pulse displayed in Figure 9 at $140 Mw/cm^2$. The peak of the transmitted pulse usually occurs within 1 nanosecond of the peak of the incident pulse.

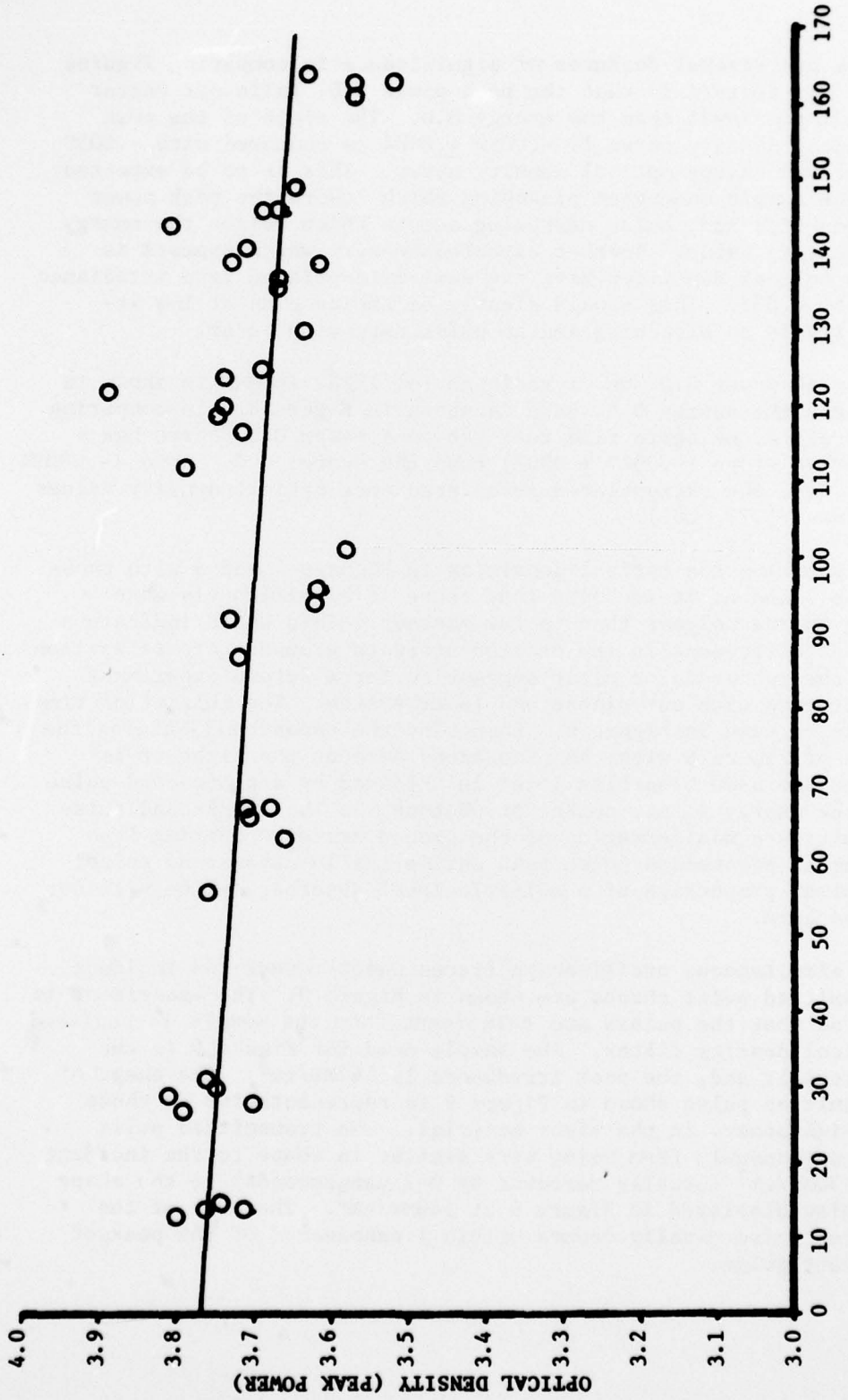

FIGURE 7. THE PEAK POWER OPTICAL DENSITY OF IR282 IN MMA VS. IRRADIANCE

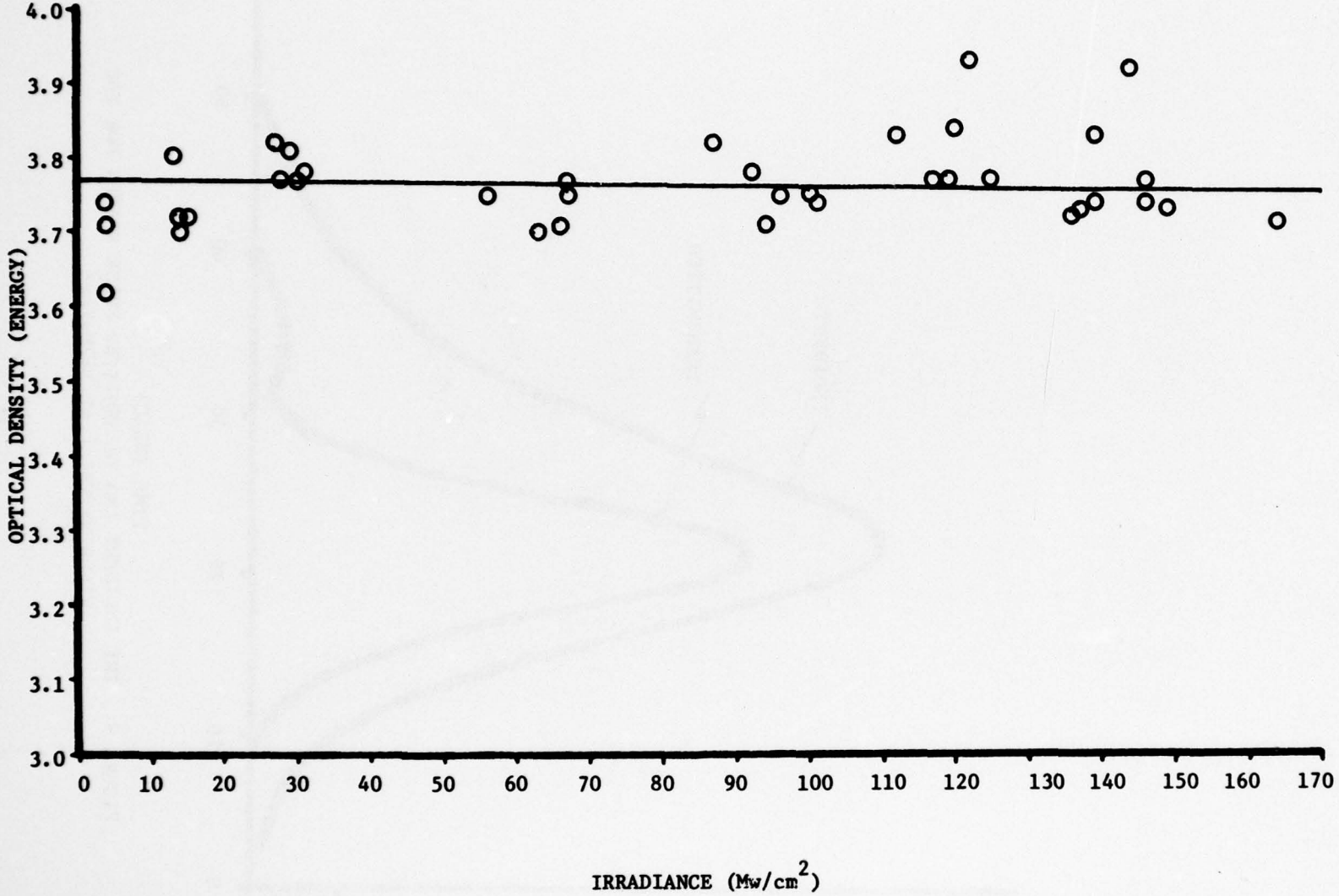

FIGURE 8. THE ENERGY OPTICAL DENSITY OF IR282 IN MMA VS. IRRADIANCE

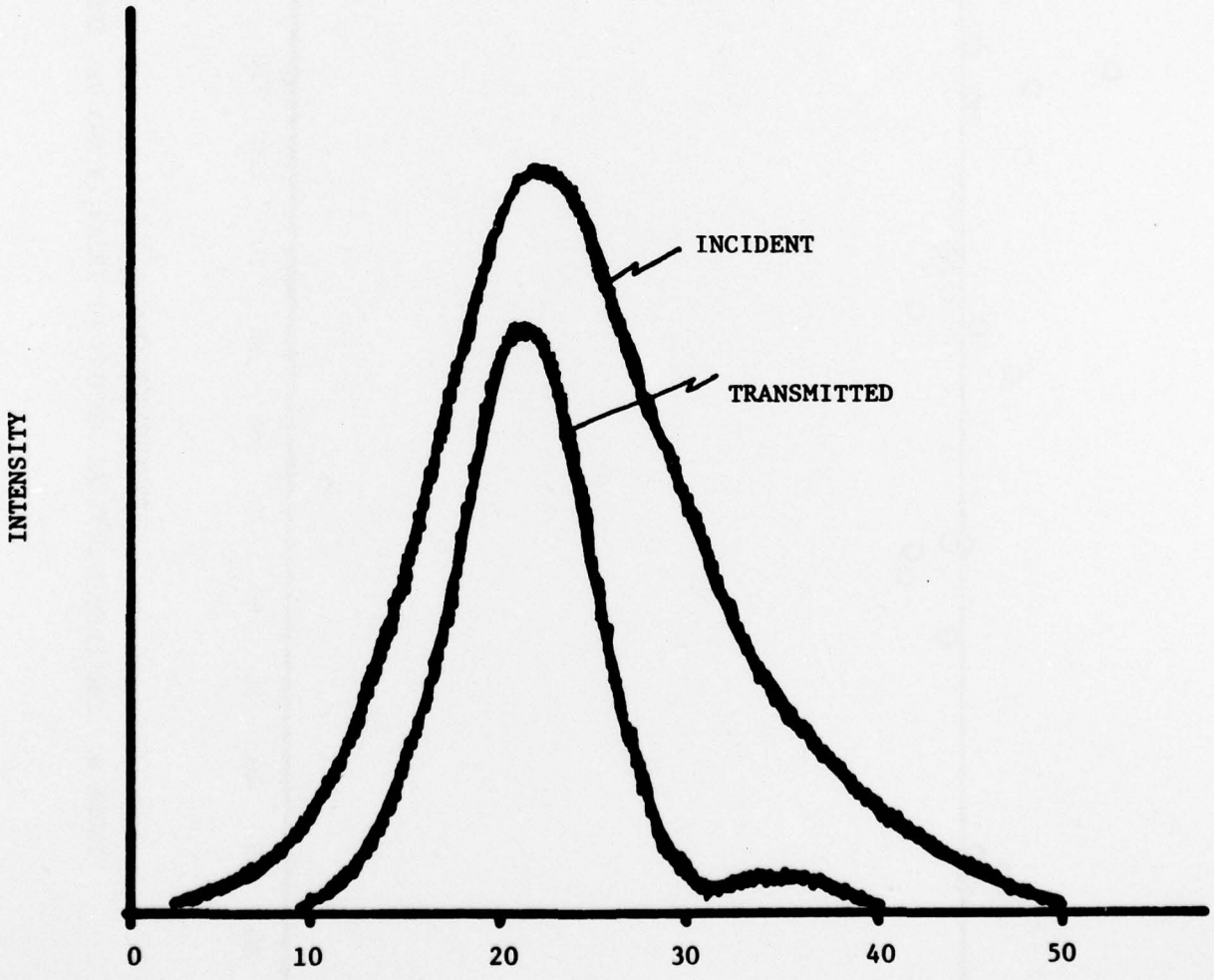

FIGURE 9. THE INCIDENT AND TRANSMITTED PULSE SHAPES FOR THE VISOR MATERIAL AT 142Mw/cm^2

In Table 1, the optical density is given for a sequence of times into the pulse. As is expected the O.D. begins at a higher value (6.45) when the irradiance is low and falls off as the irradiance increases which agrees with the data in Figure 4. A plot of the data in Table 1 is shown in Figure 10. After the peak of the pulse, the optical density increases to values higher than would be expected on the basis of Figure 4. At the tail of the pulse the optical density returns to low irradiance level values. This behavior gives rise to the secondary peak. One of the possible explanations for this behavior is that the leading edge of the pulse pumps the material into an excited state with a long enough relaxation time and a high enough extinction coefficient to increase the transient optical density. The nonlinear absorption of light pulses resulting in pulse distortions has been modeled by a variety of authors.[2-6] It is not necessary to include the details of their work here; it suffices to say that the range of pulse shapes seen within this study can be fit by the models of the above authors.

---

[2] L. Huff and L. G. DeShazer, J. Appl. Phys 40, #12, 4836 (1969).

[3] A. Zunger and K. Bar-Eli, J. Chem. Phys. 57, #8, 3558 (1972).

[4] C. R. Giuliano and L. D. Hess, J. Quant. Elec. QE-3, #8, 358 (1967).

[5] J. Herrmann, J. Wienecke, and B. Wilhelmi, Optical and Quant. Elec. 7, 337 (1975).

[6] M. Andorn and K. H. Bar-Eli, J. Chem. Phys. 55, #10, 5008 (1971)

TABLE 1

TRANSIENT OPTICAL DENSITY VALUES FOR THE PULSES SHOWN IN FIGURE 9.

TIME (NANO[illegible])	IRRADIANCE (Mw/cm^2)	OPTICAL DENSITY
0	0	--
2	2	--
4	4	--
6	7	--
8	11	--
10	20	6.45
12	34	6.12
14	55	5.94
16	77	5.81
18	107	5.69
20	133	5.61
22	142	5.63
24	135	5.72
26	117	5.91
28	98	6.17
30	78	6.53
32	60	6.53
34	47	6.41
36	37	6.26
38	29	6.27
40	19	--

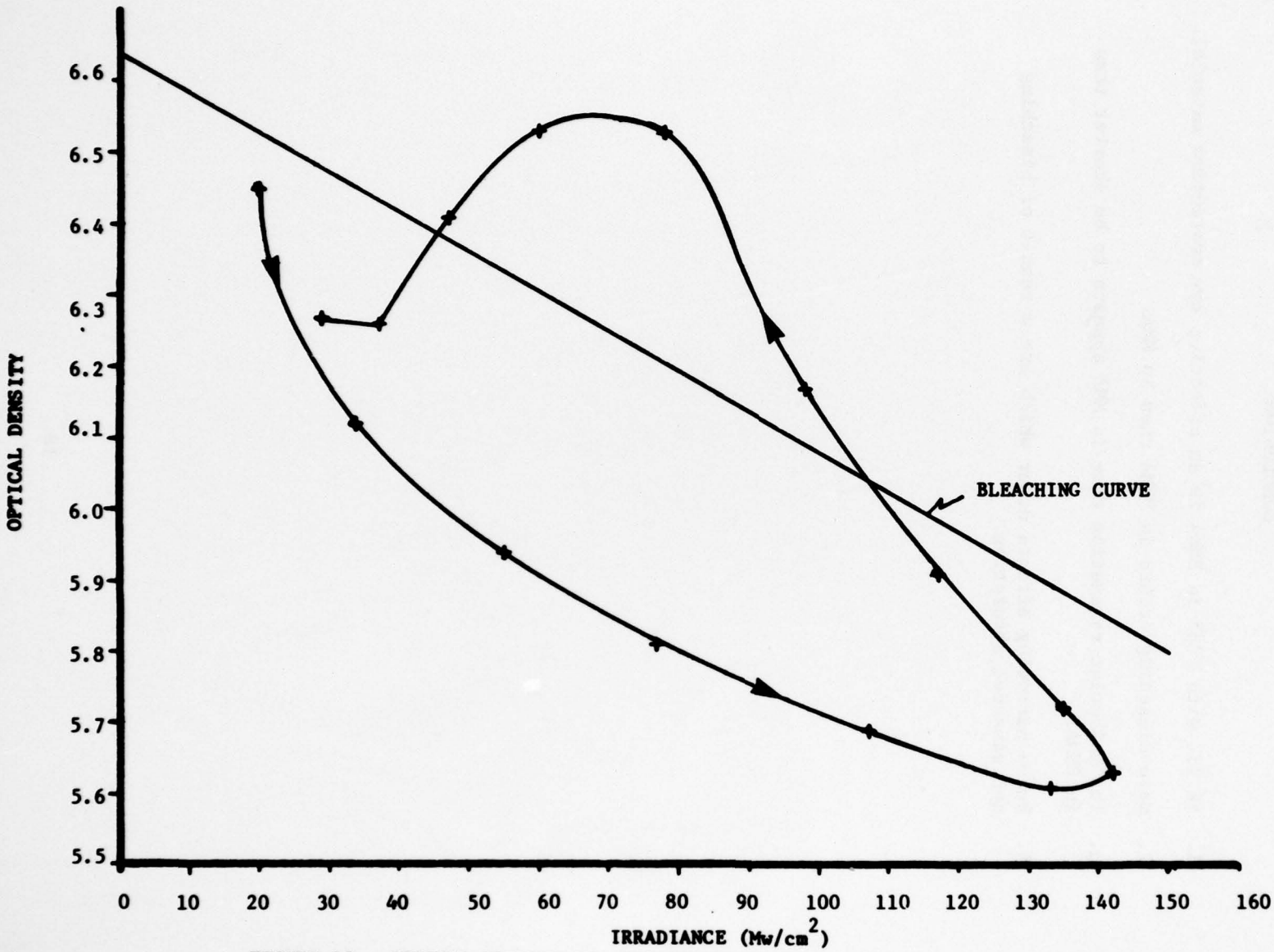

FIGURE 10. OPTICAL DENSITY VS. IRRADIANCE FOR THE TWO PULSES SHOWN IN FIGURE 9

CONCLUSIONS

1. IR 282 with K283 in PMMA is an effective eye protective material.

2. More bleaching occurs in PMMA then in MMA.

3. The molecular relaxation time in MMA appears to be shorter than in PMMA.

4. Pulse narrowing effects occur which are a result of bleaching and enhanced absorption.

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1. J. J. Mikula, W. G. Thomas, F. D. Verderame, FA Report R-1984, November (1970)

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3. A. Zunger and K. Bar-Eli, J. Chem. Phys. 57, #8, 3558 (1972)

4. C. R. Giuliano and L. D. Hess, J. Quant. Elec. QE-3, #8, 358 (1967)

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